

NIST Researcher Improves Models for Thermodynamic Properties of Industrially Important Fluids

The work described here addresses the need for “technical equations of state” suited for advanced technical applications, such as process calculations including caloric properties, for fluids where state-of-the-art measurements are not available and for which very low uncertainties are not required. The new equations are up to a factor of ten times faster with only a slight loss in accuracy.

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Equations of state are used to represent the thermodynamic properties of fluids over ranges of state conditions; accurate and consistent information on such properties as density, heat capacities, phase boundaries, compressibility, sound speed, enthalpy, etc. are required to use the fluids in thermodynamic cycles or other applications, for commerce in these fluids, and in their production or use as a feedstock. Beyond the ideal gas law, equations of state for pure fluids have progressed over the years from simple cubic and virial equations of state to Beattie-Bridgeman, Benedict-Webb-Rubin (BWR), modified BWR (mBWR) equations and most recently to fundamental equations of state that are explicit in the Helmholtz energy. Most modern, high-accuracy equations of state for pure fluid properties are explicit in the Helmholtz energy as a function of density and temperature. All single-phase thermodynamic properties can be calculated as derivatives of the Helmholtz energy. During the past 20 years or so, many of the industrial equations of state for fluids such as nitrogen, carbon dioxide, R-134a, and water have been replaced with high-accuracy fundamental equations of state developed from fitting state-of-the-art experimental measurements for density, phase equilibrium, heat capacity, and speed of sound. There are about 30 fluids that fit into this category; most of these fluids are fully characterized over the entire fluid surface by extensive experimental measurements. However, many fluids of industrial interest do not have an extensive set of experimental data to facilitate the development of high-accuracy, fundamental equations of state.

The NIST work addresses the need for “technical equations of state” suited for advanced technical applications, such as process calculations including caloric properties, for fluids where state-of-the-art measurements are not available and for which very low uncertainties are not required. Unlike highly accurate equations, which generally use 20 to 50 fluid-specific

terms to describe densities to the order of (0.01 to 0.1) %, we developed “technical equations” that are shorter and often use fixed functional forms to characterize the fluid properties. Although the new technical equations suffer from a slight loss in accuracy, their shorter forms allow for faster computations – from 2 to 10 times faster depending on the number of terms in other equations and on the use of special terms for increasing the accuracy. In this work, we developed technical equations of state for 20 industrially important fluids, shown in Table 1.

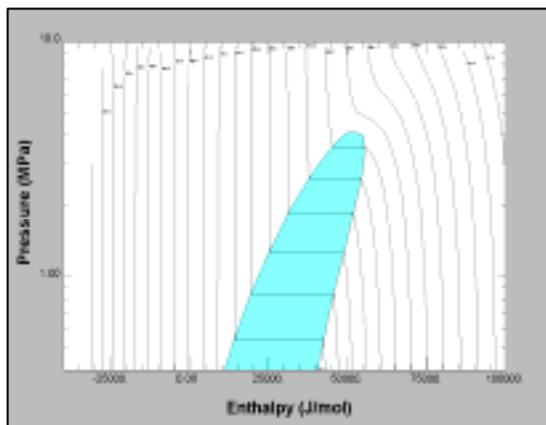
Table 1. Summary of industrial fluids covered in the present study

| | | | |
|------------------|-----------------|------------------|-------------------|
| acetone | carbon monoxide | carbonyl sulfide | decane |
| hydrogen sulfide | isopentane | neopentane | isohexane |
| krypton | nitrous oxide | nonane | sulfur dioxide |
| toluene | xenon | hexafluoroethane | octafluoropropane |
| R-141b | R-142b | R-245fa | R-41 |

NIST developed Equations of State for 20 industrially important compounds for which state-of-the-art process calculations were not available. The shorter “technical equations” provide much faster computations with the appropriate level of accuracy needed.

For several fluids, the new equations presented here are the first attempt to depict the fluid's properties with multiparameter equations. For other fluids, the new equations replace older ones, many of which showed unphysical behavior such as calculated negative heat capacities at low temperatures, or that exhibited physically impossible behavior in accessible single-phase regions of the fluid surface. Typical uncertainties of properties calculated with the new equations of state are 0.2 % in density, 1-2 % in heat capacity and liquid phase speed of sound, and 0.2 % in vapor pressure. We also have implemented the

correlations into NIST Standard Reference Database 23 (NIST REFPROP), where users can easily generate graphical output useful in engineering applications such as *the pressure-enthalpy diagram shown in Figure 1.*



Impact: These correlations are important to both our infrastructural work (information will be disseminated through such standard reference databases as NIST REFPROP), and to the immediate needs of customers. The article describing the work was the most accessed manuscript for the second quarter of 2006 for the Journal of Chemical and Engineering Data.

Future Plans: The ongoing program of advanced equation of state development will continue to focus on both immediate and specific demands for improved property information for important industrial fluids.

Publications:

These correlations have been published recently (Lemmon, E.W. and Span, R., "Short Fundamental Equations of State for 20 Industrial Fluids", J. Chem. Eng. Data **2006**; 51(3); 785-850)